SYNTHESIS AND CHARACTERIZATION OF ZEOLITES FROM SODIUM ALUMINOSILICATE SOLUTION

by

SITI AIDA BINTI IBRAHIM

Thesis submitted in fulfillment of the requirements for the degree of Master of Science

August 2007

ACKNOWLEDGEMENTS

Thank you to Allah for His Blessing and giving me an ability and strength to complete this thesis.

Firstly, I would like to express my deepest gratitude to my supervisor Dr. Norlia Baharun for her expert guidance, constant attention, valuable suggestions, enthusiastic support and personal concern during the research and through the course of my study. Her fruitful ideas throughout the research project has helped me accomplished this work successfully.

Special thanks to the Dean of School of Material and Mineral Resources Engineering, Associate Professor Dr. Khairun Azizi Azizli for her permission to let me use all the brilliant facilities and equipment in completing my project. Under her leadership, she has created a healthy learning environment in the school. I would also like to extend my sincere appreciation for all the lecturers in the school especially to Associate Professor Dr. Azizan Aziz for his support and guidance throughout my study. I would like to thank the technical staffs of School of Materials and Mineral Resources Engineering, especially to Mdm. Fong Lee Lee, Mr. Shaarani, Miss Mahani and Mr. Hasnor for their various contributions in one way or another.

To my dear friends, Nurul'Ain, Norwanis, Roshazita , Faizul, Shahrizam, Suhaina, Dr. Hasmaliza, Dr. Zuhailawati and all close members of postgraduate room of School of Materials and Mineral Resources Engineering, thank you for making my life in USM so colorful and enjoyable. The memory of our friendship will forever stay inside my heart.

Last, but not least to my family especially to my ever-loving mother whom are always on my side, Hajjah Rinah Binti Mohd. Jirin, Thank you for the support and the encouragement you gave me to pursue my dreams. Not to forget, my family members who always be there for me through my thick and thin.

May ALLAH bless all of us and only HE, the Almighty could repay all my debts to all of you.

Wassalamu'alaikum warahmatullah wabarakatuh.

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LIST OF SYMBOLS

°C	Celcius
Å	Angstron (1×10^{-10})
nm	nanometer (1×10^{-9})
µm	micrometer (1×10^{-6})
cm	Centimeter (1×10^{-2})
cm^3	Centimeter cube
mg	milligram
g/l	gram /liter
g/cm^3	gram/centimeter cube
M	molar
meq/100g	Milliequivalents/100gram

LIST OF ABBREVIATION

NaOH	Sodium Hydroxide
SiO_2	Fumed Silica
$NaAlO_2$	Sodium Aluminate Anhydrous
HCl	Hydrochloric Acid
H_3BO_3	Boric Acid
MgO	Magnesium Oxide
Na_2CO_3	Sodium Carbonate Anhydrous
H_3BO_3	Boric Acid
CH_3COONH_4	Ammonium acetate
CH_3OH	Methyl Alcohol
N_2	OFN gas (oxygen free nitrogen)
$C_{21}H_{14}Br_4O_5S$	Bromocresol green indicator
KBr	Potassium Bromate
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
BET	Brunauer, Emett and Teller
CEC	Cation Exchange Capacity
FTIR	Fourier Transform Infrared Spectrophotometer
VPT	Vapor Phase Transport
PSD	Particle size distribution
FAU	Faujasite
SOD	Sodalite
GIS	Gismondine
LTA	Lynde Type A

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SINTESIS DAN PENCIRIAN ZEOLIT DARIPADA LARUTAN NATRIUM ALUMINOSILIKAT

ABSTRAK

Rangkaian siri sintetik zeolit telah berjaya disintesiskan daripada larutan natrium aluminosilikat dengan kepekatan Si dari 1 hingga 8 molar menggunakan habuk halus silika (fumed silica) dan natrium aluminat. Kesan daripada tertib percampuran sumber sintesis dan penggunaan pelbagai kepekatan Si terhadap penjelan, penghabluran, fasa, ciri kimia-fizikal dan morfologi yang terhasil dilaporkan. Data daripada pemantauan in-situ perlakuan gel natrium aluminosilikat dan masa penghabluran yang terhasil pada suhu bilik turut dilaporkan dalam kajian ini. Keputusan XRD menunjukkan kehadiran fasa zeolit dengan kerangka kerja sama seperti FAU, LTA, SOD, dan GIS dalam sintetik zeolit yang disintesiskan dengan saiz kristalit dianggarkan antara 3 hingga 20nm. Ciri-ciri kimia-fizikal sintetik zeolit pula diperolehi daripada analisis saiz partikel Malvern, BET dan FTIR. Daripada analisis Malvern, purata saiz partikel (d_{50}) adalah dari 12 hingga 95 mikron manakala analisis BET memberikan luas permukaan sintetik zeolit yang tertinggi pada 9.84m^2/g. Spektra FTIR pula membuktikan kehadiran getaran dalaman merujuk kepada Si-O-(Si) dan Si-O(Al) dalam struktur tetrahedranya pada julat getaran 1200-400cm^{-1}, manakala kehadiran air dalam zeolit ditunjukkan dalam julat getaran 1600-3700cm^{-1}. Spektra FTIR juga menunjukkan wujudnya getaran kekisi-pseudo (pseudo-lattice) dalam struktur unit sintetik zeolite iaitu pada julat 500-700cm^{-1}. Kajian morfologi permukaan daripada fotomigrograf SEM menunjukkan serbuk sintetik zeolit yang terhasil mempunyai struktur berbentuk lamela dangan pinggir sisinya berbentuk kubik. Saiz kristal pula dianggarkan berada antara 1 hingga 12 mikron. TEM fotomikrograf menunjukkan kehadiran liang-liang halus dengan anggaran saiz liang adalah 13 hingga

23nm (lebar) dan 18 hingga 43nm (panjang). Akhir sekali, nilai CEC tertinggi yang diperolehi bagi zeolit yang disintesiskan adalah pada 66.3meq/100g dan nilai yang paling rendah pula pada 7.65meq/100g dengan masa kontak selama 12 jam.

SYNTHESIS AND CHARACTERIZATION OF ZEOLITES FROM SODIUM ALUMINOSILICATE SOLUTION

ABSTRACT

A series of synthetic zeolites were successfully synthesized from sodium aluminosilicate solutions with varying Si concentration from 1 to 8 molar using fumed silica and sodium aluminate. The order of mixing and the effect of varying amount of Si in the sodium aluminosilicate solution towards gelation, crystallization, phases, physico-chemical characteristics and surface morphology were studied. Data

concerning the in-situ monitoring of sodium aluminosilicate gelation behavior and the crystallization time at room temperature are reported. XRD results showed that the phases of zeolites synthesized are similar to FAU, LTA, SOD and GIS framework. The crystallite size was found to vary from 3 to nearly 20 nm. The physico-chemical characteristics of the product were obtained from Malvern particle size analyzer, BET and FTIR. From Malvern analysis, it was found that the average particle sizes (d_{50}) of synthetic zeolites were varied from 12 micron to 95 micron while the highest surface area values obtained from BET was about 9.84 m^2/g. Meanwhile, FTIR spectra exhibited the presence of internal Si-O-(Si) and Si-O-(Al) vibrations in the tetrahedra or alumino- and silico-oxygen bridge in the range of 1200 – 400 cm^{-1}, while the presence of zeolite water in the range of 1600- 3700 cm^{-1} and the pseudo-lattice vibrations of structural unit in the range of 500-700 cm^{-1}. Surface morphological studies obtained from SEM photomicrographs showed the powdered synthetic zeolite have a lamellar structure with cubical edge and the crystal size was estimated to be 1 to 1.2 micron. TEM photomicrographs showed the presence of pores with the pore sizes estimation at 13-23 nm (width) and 18-43 nm (length). Finally, the highest CEC value of the synthesized zeolites against ammonium was obtained at 66.3 meq/100g meanwhile the lowest was at 7.65 meq/100g at optimum contact of 12 hours.

CHAPTER 1

INTRODUCTION

1.1 Background

Malaysia is now at the mid point of its journey towards becoming a developed country by 2020. Since the global environment is changing, the Prime Minister, Datuk Seri Abdullah Ahmad Badawi has announced that the nation needs to improve and upgrade the country's domestic condition (Ninth Malaysia Plan, 2006). The National Mission is presented by the government as a policy and implementation framework that outlines the country's priorities for the next 15 years along with the Ninth Malaysia Plan. One of the objectives in the National Mission is to move the economy up to the value chain. It is noted that to be successful in the increasingly competitive global market, Malaysia must move out from its "middle development" stage towards human capital driven economy. This can be achieved by several step listed in the National Vision which one of it is to increase the productivity, competitiveness and value add of the established activities in agriculture, manufacturing and service sector. Even though it is necessary for the nation to move up the economy value chain, the needs to balance between the development needs and the environment must be maintained. This can be achieved by better management in environment stewardship since a better quality environment will contribute towards improving the quality of life.

During the Eight Plan Period, the government have emphasized on improving environmental quality through better management particularly in air and water quality, solid waste management as well as the utilization of cleaner technologies. Nowadays, through the advancement of modern science and technology, zeolites can contribute to a cleaner, safer environment in a great numbers of ways (Bell, 2001). In powder

detergents, zeolites have replaced the harmful phosphate builder, which have been banned in many countries due to the water pollution risks. In petroleum and hydrocarbon industry, the chemical process can be more efficient with zeolite acting as the catalyst, thus saving the energy and indirectly reduced the pollution. The processes can be carried out in a fewer step and minimizing unnecessary waste and by-products. Furthermore, zeolite can also act as solid acids which could reduce the need for corrosive liquid acids and as redox catalyst and sorbents where they can remove atmospheric pollutants such as engine exhaust gases and ozone depleting CFCs (Monticelli et al., 1999 and Chatterjee et al., 2003). Zeolite can also be used to separate harmful organics from water (Wang et al., 2006 and Park et al., 2002) and removing heavy metal ions including those produced by nuclear fission from water (Nah et al., 2006 and Ursini et al., 2006).

Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals with fully cross-linked open framework structures made up of corner sharing SiO_4 and AlO_4 tetrahedra. There are about 40 natural zeolites which have been identified during the past 200 years and more than 150 zeolites have been synthesized. The most common of natural zeolite are analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite while as for synthetic zeolites; the most common are zeolites A, X, Y and ZSM-5. Both natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve and catalytic properties.

The naturally occurred zeolite is formed as a result of the chemical reaction between volcanic glass and saline water. The temperatures favoring the natural reaction are ranges between 27°C to 55°C with pH between 9 and 10. However, nature requires 50 to 50,000 years to complete the reaction with rarely phase-pure state of zeolite. This type of zeolites are contaminated to varying degrees by other minerals such as Fe^{2+}, quartz, SO_4^-, other zeolites and amorphous glass.

Synthetic zeolites on the other hand, hold some advantages over their natural analogs. The synthetics can, of course, be manufactured in a uniform phase-pure state. It is also possible to manufacture desirable structure which does not appear in nature such as zeolite A. Since the principal raw materials used to manufacture zeolite are silica and alumina, which are among the abundant mineral components on earth, the potential to supply zeolite is virtually unlimited. Finally, zeolites manufacturing processes engineered by humankind require significantly less time than 50 to 50,000 years as prescribed by nature.

In year 1974, Breck, have declared that rarely in our technology society does the discovery of a new class of inorganic materials results in such wide scientific interest and kaleidoscopic development of applications as what happened with the zeolite molecular sieve. The declaration was 30 years ago after the commercial introduction of synthetic zeolites. During that time, the number of areas utilizing zeolites had grown phenomenally. Since then, the variety of applications and zeolites types available has continued to increase.

As zeolites are already well established in such environmentally driven applications, therefore, it is used as phosphate-free ion exchangers for detergent water softening and as the production of lead-free octane enhancer for gasoline. Not only that, zeolite is also well-known used as ammonia and ammonium removal in water, and other heavy metal removal in wastewater since it has a capability as ion exchanger. Today, zeolites are being considered for a variety of important environmental services. To put the potential zeolites into perspective, this research work looks at the properties of zeolites and how the material is synthesized.

1.2 Importance of Research

A considerable research and development effort is being made to produce a tailor made zeolite synthesis. This is because natural zeolites are rarely in phase-pure zeolite and contaminated to varying degrees of other minerals such as quartz, SO_4^- and amorphous glass. Thus, for this reason, natural zeolites are excluded from many important commercial applications where uniformity and purity are essential. On the other hand, synthetic zeolite could be manufactured in a uniform phase-pure state. Furthermore, it is also possible to engineer a desirable structure zeolite which does not appear in nature such as Zeolite A and ZSM-5.

By better understanding on the mechanism responsible for its formation from its precursor, a tailor made zeolite synthesis could be manufactured. It is necessary to know the mechanism process since a desirable structure zeolite can be engineered due to its application. The changes made in synthesis process can affect the structure and type of zeolite produced. As an example, the varying degrees of Si concentration and the source of Si used can produce a different type of zeolite. Therefore, it is necessary to have a vast knowledge on its fundamental process because a specific tailor made zeolite is depended on its application whether used as ion exchanger for water and wastewater treatment or as catalyst used in hydrocarbon industry.

The type of cation present not only influences the ion-exchange properties of zeolite, but also is a factor in its adsorptive and catalytic properties. High purity synthetic zeolites exhibit uniform pore sizes that can be further tailored to specific molecular dimensions by changing the nature of the cation after synthesis. For example, the greatest volume use for zeolite is due to their ion exchange properties. As we know, hard water causes poor performance in laundry

detergents. Zeolite A with Na^+ cations is widely used in laundry detergent as a replacement for environmentally undesirable phosphates as detergent water softener. Another example is the used of zeolite in the removal of ammonium in water and wastewater. Therefore, the production of zeolite from sodium aluminosilicate can contribute to a cleaner environment where the stewardship towards waste management is maintained since the applicability of the zeolite acting as ion exchanger (for the removal of an ammonium and other heavy metal in water or wastewater) is widely known.

1.3 Objective of the research

The aim of this research was to study the structure and properties of zeolite synthesized from aluminosilicate solutions and gels. To achieve this, a study was carried out with the following objectives:

i. To synthesize zeolites from sodium aluminosilicate solution via hydrothermal sol gel process.
ii. To study the effect of varying Si concentration and the sequence of mixing order in the solution towards the development of zeolite crystallization.
iii. To examine the characteristic of the synthetic zeolite produced (i.e. morphology, physico-chemical and phases identification) via SEM, TEM, FTIR , XRD and others
iv. To evaluate the potential of the produced synthetic zeolite on its capacity as an ion exchanger.

1.4 Scope of the research

Due to the industrial important of zeolite, much effort is made to unravel the mechanism responsible for its formation from its precursors. The art of creating zeolite synthesis has become a scientific interest because the process can be engineered to produce a tailor made synthesized zeolite. In zeolite synthesis, the needs to imitate the natural geological process are necessary. However, it is not possible since zeolite formation took thousands of years while commercially, zeolite must be produced in hours or days. Therefore, the scientist must replicate the best condition of zeolite synthesis to achieve the desirable zeolite with certain properties within a shorter time. The use of hydrothermal process in zeolite synthesis is one of the major interest techniques adopted by the scientist. This is mainly due to the lower production costs and convenience for approach.

The major aim of the work presented in this thesis is to investigate the synthesis of zeolites from sodium aluminosilicate solution. The synthesis was carried out by sol-gel process and under the confined hydrothermal condition at a temperature of 80°C for two weeks. In this study, the sodium aluminosilicate solution was prepared using silicate solution (at varying amount of Si), aluminate solutions (amount of Al remains constant) and sodium hydroxide (NaOH) solution. The presence of NaOH was to create a caustic environment for the synthesis process. The solid is separated by filtration, washed several times with distilled water and then dried overnight at 50° - 60° C to a constant weight. At the end of the process, the solid product was recovered for further characterization and analysis.

In this study, the investigation on the effect of varying Si concentration (1 to 8 molar) and the sequence of mixing order in the zeolite produced has been carried out. The gelation and the crystallization time of zeolite are measured to study the influence

of Si/Al ratio and the sequence of mixing order. Studies on the surface morphology of the zeolite produced are carried out via SEM and TEM while the identification of mineral phases are carried out by using XRD. The physico-chemical properties of synthetic zeolite such as the specific surface area, density, particle size and lattice vibration are obtained with BET, Particle Size Analyzer (Malvern) and FTIR respectively. The cation exchange capacity (CEC) value was also determined using standard procedures. Details explanation of these experimental procedures was discussed in Chapter 3.

This research was conducted according to the method that had been used by Harvey and Glasser (1989). Some modifications have been made for the synthesis conditions where by different ratios of Si/Al, the type of inorganic cation and the amount of alkali concentration (NaOH) were used. A study on the CEC values has also been done to evaluate the potential of synthesized zeolite for ammonium removal.

CHAPTER 2

Literature Review

2.1 Introduction

Zeolite are crystalline aluminosilicates containing pores and channels of molecular dimensions that are widely used in industry as ion exchange resins, molecular sieves, sorbents and catalysts. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. Many occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic, and are made commercially for specific uses, or produced by research scientist trying to understand their chemistry.

The zeolite history began with the discovery of stilbite by Crönstedt, a Swedish mineralogist in year 1756. Upon heating the zeolite released occluded water, which gave the materials their general name, zeolite, after the Greek words, "ξειν" (*zeo*) , to boil, and "λιθος" (*lithos)*, stone. A representative empirical formula of a zeolite is

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O \qquad (2.1)$$

where M represents the exchangeable cation of valence n. M is generally a Group I or II ion, although other metal, non-metal and organic cations may also balance the negative charge created by the presence of Al in the structure. The framework may contain cages and channels of discrete size, which are normally occupied by water (Ghobarkar et al., 1999).

There are about 40 natural zeolites that have been identified during the past 200 years. The most common are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. There are also more than 150 zeolites that have been synthesized and the most common are zeolites A, X, Y, and ZMS-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

2.2 Structure

Zeolite structure contains two types of building units namely, primary and secondary. A primary building unit (PBU) is the simpler building compared to secondary one. This is because, in PBU, a tetrahedron of (TO_4) of 4 oxygen ions surrounding a central ion of either Si^{4+} or Al^{3+}. These PBU are linked together to form a three-dimensional framework and nearly all oxygen ions are shared by two tetrahedral. Zeolite framework is based on an extensive three dimensional network in which the polyhedral sites, usually tetrahedral, are linked by oxygen atoms.

Different combinations of the same secondary building unit (SBU) may give numerous distinctive structural polyhedra formed from smaller ring units. The net negative charge on the framework is balanced by the presence of the cations in most cases Ca, Na or K, which are situated in cavities within it. The zeolite framework is almost structurally independent of the (Na, Ca, K) cations and as the latter do not fill all the cavities replacement of the type Ca↔2 (Na, K) can also occur. Figures 2.1 and 2.2 show the basic structure of zeolite framework. The complexity of zeolites structure is due to the various ways in tetrahedral group which are linked by the common sharing of oxygen ions to form polynuclear complexes. As listed in Table 2.1, a considerable

variation in the chemical composition results from the substitution of cations. Due to this, they give rise to zeolite and zeolite like materials of a very wide diversity.

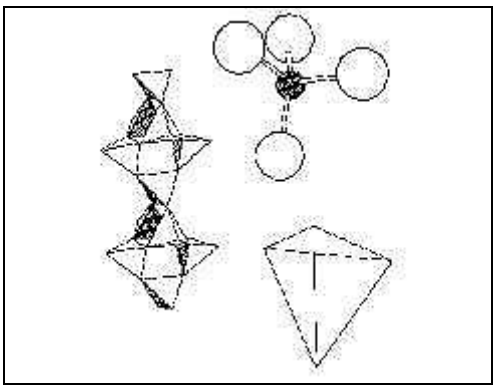


Figure 2.1. Basic structure of zeolite frameworks (Byrappa and Yoshimura, 2001)

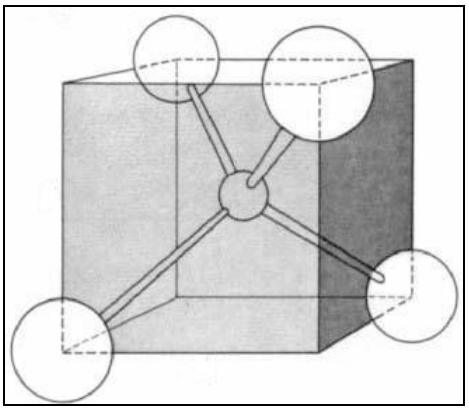


Figure 2.2. Basic structure of zeolite frameworks (Byrappa and Yoshimura, 2001)

Table 2.1. Coordination of cation with oxygen in silicate structures (Byrappa and Yoshimura, 2001)

Ion	Radius (Å)	Radius Ratio	Coordination No.	Bond Strength
B^{+3}	0.20	0.20	3, 4	1 or $^3/_4$
Be^{+2}	0.31	0.25	4	$^1/_2$
Li^{+}	0.60	0.34	4	$^1/_4$
Si^{+4}	0.41	0.37	4, 6	1
P^{+5}	0.34	0.34	4, 6	$^5/_4$ or $^5/_6$
Al^{+3}	0.50	0.41	4, 5, 6	$^3/_4$ or $^1/_2$
Ge^{+4}	0.44	0.43	4, 6	1 or $^2/_3$
Ga^{+3}	0.62	0.46	4, 6	$^3/_4$ or $^1/_2$
Mg^{+2}	0.65	0.47	6	$^1/_3$
Na^{+}	0.95	0.54	6, 8	$^1/_6$ or $^1/_8$
Ca^{+2}	0.99	0.67	7, 8, 9	$^1/_4$
K^{+}	1.33	0.75	6, 7, 8, 9, 10, 12	$^1/_9$
NH_4^{+}	1.50	0.85	9, 12	$^1/_9$ or $^1/_{12}$

There are some simple criteria that are used to establish the zeolite frameworks. The most important one is the framework density (FD), which means the number of T-atoms (temperature atoms) per 1000°A^3. The distribution of these values for the porous and dense frameworks whose structures are well established is showed in Figure 2.3(a) and (b). Thus, the FD is obviously related to the pore volume, but does not reflect the size of the openings and to some extent it depends on the composition for the structural and chemical reason.

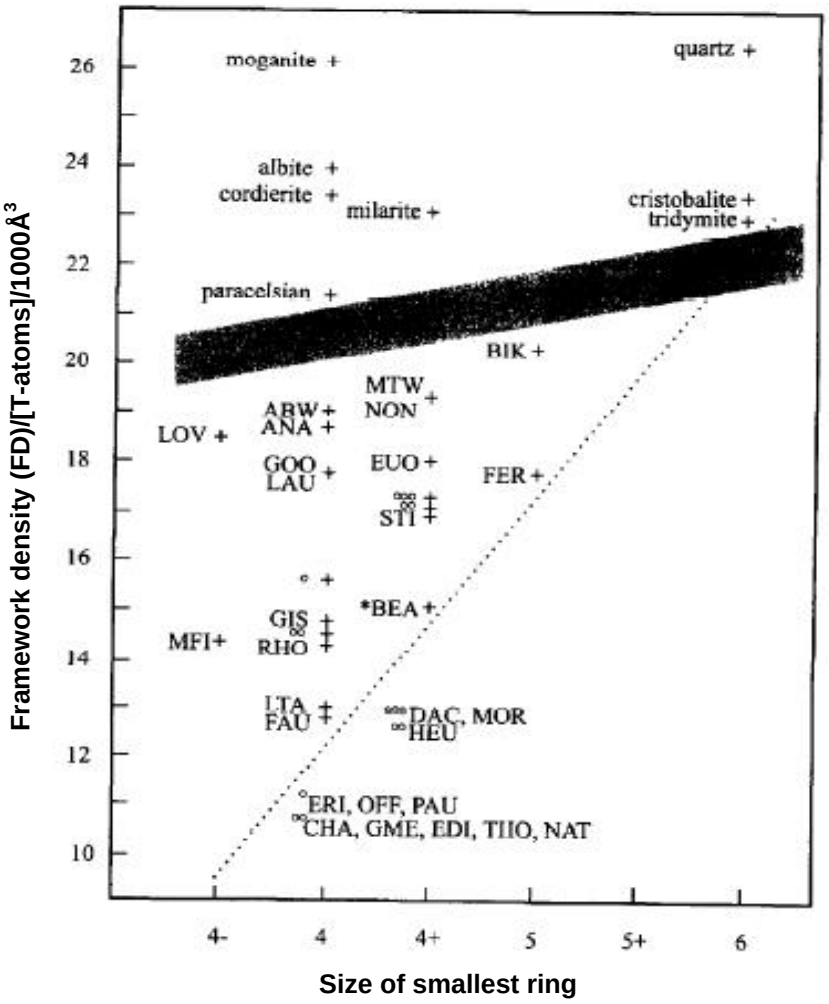


Figure 2.3. (a) Framework density of selected zeolites in respect to normal tectosilicates (Ghobarkar et al., 1999)

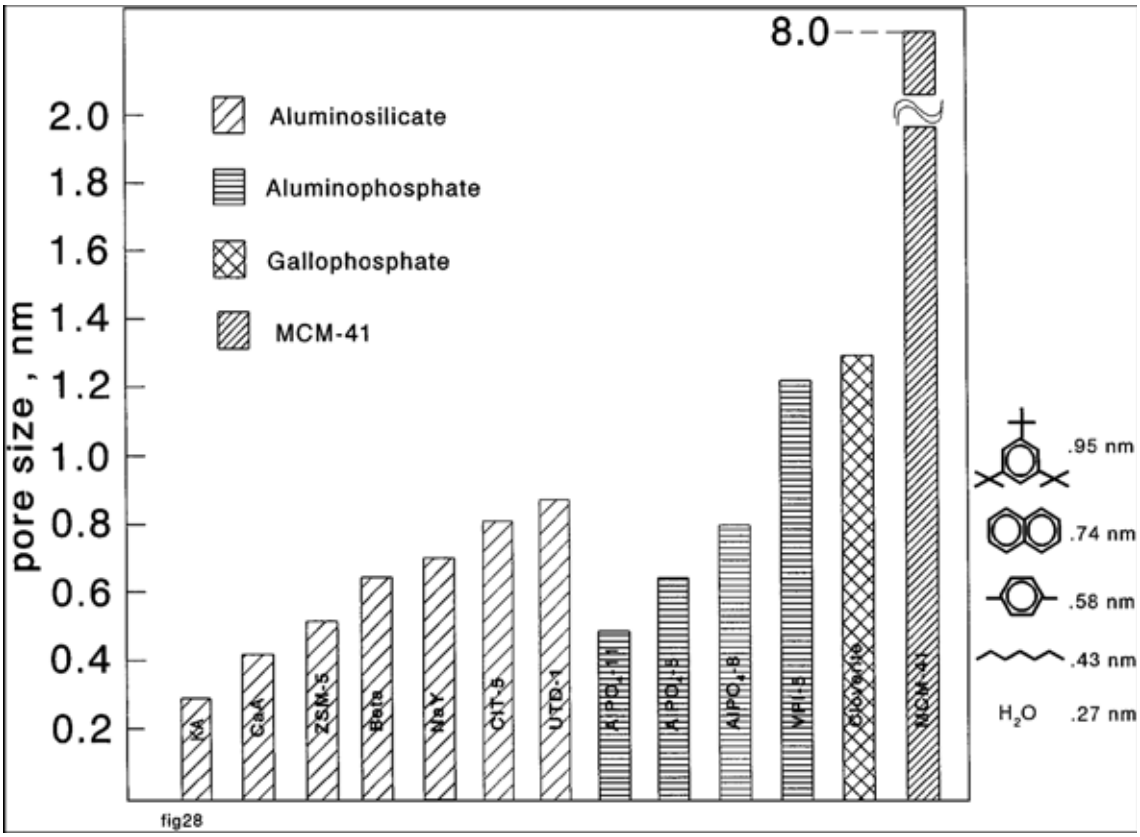


Figure 2.3. (b) Pore sizes of zeolites and ALPOs (Van der Waal and Bekkum, 1998)

Figure 2.4 shows the development of zeolite structure as follows: the primary building $(SiO_4)^{4-}$ tetrahedron (Figure 2.4a) and the tetrahedral are connected through their corners of shared oxygen atoms to form a wide range of small secondary building as in Figure 2.4b. In Figure 2.4c, a wide range of polyhedra is formed due to the interconnection of the building units. In turn, it is connect to form the extended frameworks of the various specific zeolite crystal structures. Figures 2.4a-d shows the structure of zeolites, the corners of the polyhedra represent Si or Al atoms and the connecting lines represent the shared oxygen atoms. Individual structures may comprise only one basic unit or many of them such as mineral paulingite which contains five such polyhedra.

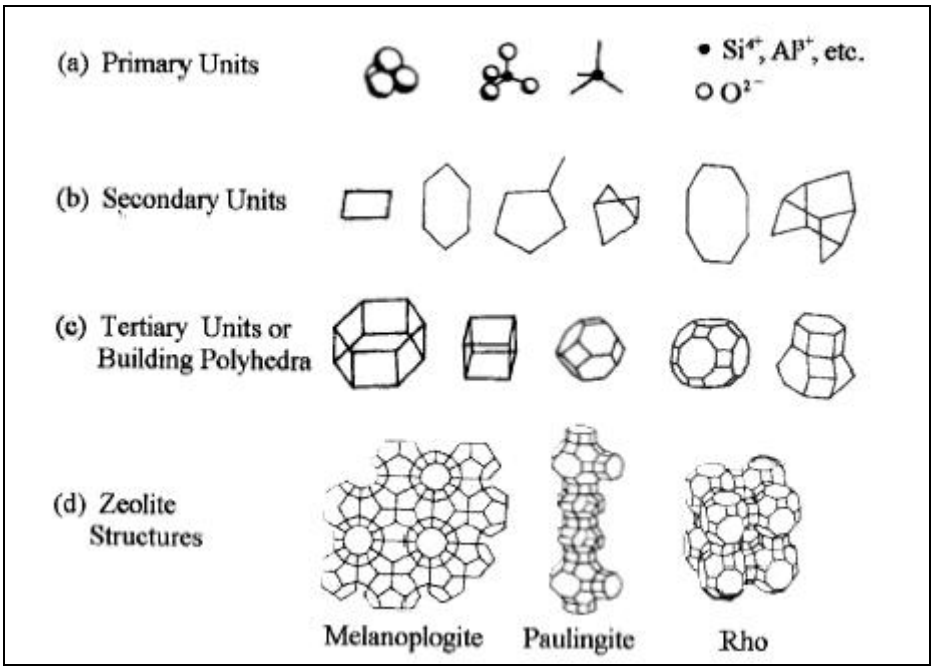


Figure 2.4. Development of zeolite structures (Byrappa and Yoshimura, 2001)

The same secondary building unit but with different combination may give numerous distinctive zeolite structures. Figure 2.5 shows an example of three different zeolites that have the same structural polyhedron (cubo-octaheron) but probably form from smaller ring units.

In accordance with the IUPAC recommendations on the chemical nomenclature of zeolites and related materials, topologically distinct framework types are represented by a mnemonic code consisting of three capital letters. This is subjected to review and clearance by the IZA Structure Commission according to a decision of the IZA Council, where took place at 7th IZC in Tokyo in 1986 (Byrappa and Yoshimura, 2001). Generally, these codes derived from the name of the type species for example FAU for faujasite or SOD for sodalite. These symbols describe all variants of a framework with a given topology, irrespective of composition, Si, and Al distribution, cell dimension and symmetry.

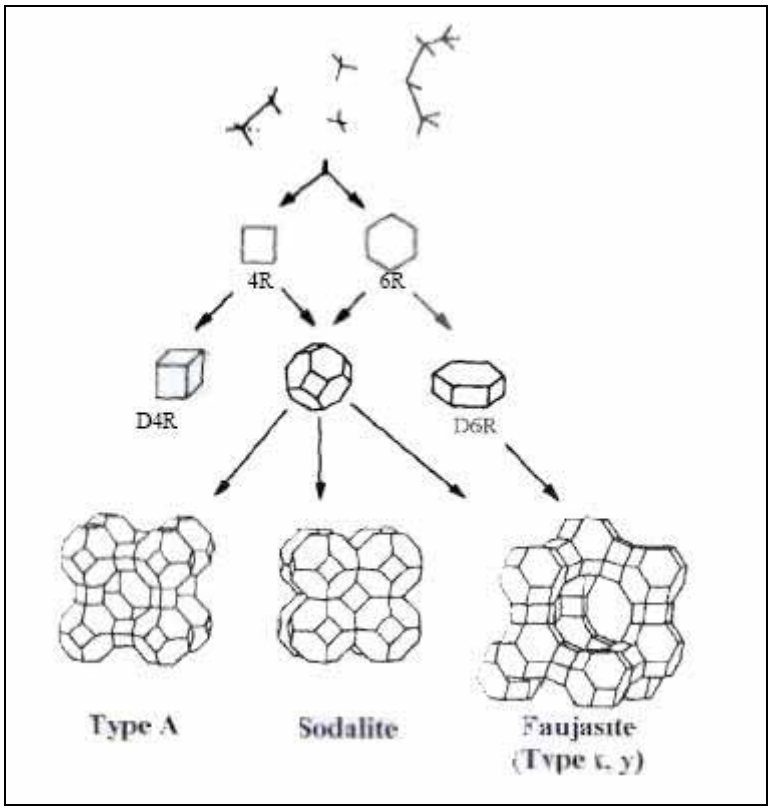


Figure 2.5. Three different zeolites (Byrappa and Yoshimura, 2001)

2.3 Properties

Mineral species such as zeolite has unique properties which are dependent upon its crystal structures and thus the type of inner cavities such as the pores, their size and form. Many of these properties are especially desirable for environmental protection, such as cation exchange capacity, adsorption properties, acid stability, ammonium capacity and wet attrition resistance. In Table 2.2, we can see a microporous solid with a broad range of physico-chemical properties of zeolites and related materials, such as phosphate-based molecular sieves. Table 2.3 briefly the description of each type of common zeolites properties.

Table 2.2. Physico-chemical properties of zeolite and molecular sieves. (Byrappa and Yoshimura, 2001).

Property	Range
Pore size	~4–13Å
Pore shape	Circular, elliptical
Dimensionality of pore system	1-D, 2-D, 3-D
Pore configuration	Channels, cages
Surface properties	Hydrophilic, hydrophobic (high silica)
Void volume	Less than ~50%
Framework oxide composition	Si, Al, P, Ga, Ge, B, Be, Zn : minor Ti, Fe, Co, Cr, V, Mg, Mn : minor

Table 2.3. Physical properties of four types of zeolite (Chen, 2001)

Type	Isotypes	Pore window (free diameter)	Si/Al ratio	Pores/ Channels
LTA	A zeolite	8-ring : 0.41 nm	~ 1	3D Spherical 1.14nm cavities
FAU	X zeolite Y zeolite	12- ring : 0.74 nm	1 – 1.5 (X) 1.5 – 3 (Y)	3D Spherical 1.18nm cavities
MOR	Mordenite	12 ring : 0.70 nm	5 - 20	2D Straight 0.70nm channels
MFI	ZSM-5 Silicalite-1	10-ring : 0.60 nm	~ 30 (ZSM-5)	3D Straight 0.60nm channels with 0.90nm intersection cavities.

In connection with the structures of the zeolite, the Si/Al ratio determines a number of important properties useful for adsorption, catalysis and ion exchange. The trend in these properties as a function of their initial Si/Al ratio for a number of zeolite is summarized in Table 2.4. For several zeolites, Si/Al ratios ranging from this initial (minimum) value to infinity can be realized by dealumination procedures. For example, in silicalite-1, it applies to a zeolite with MFI structure but without Al^{3+} ions in its framework. However, silicalite-1 does not meet the definition of zeolite due to the lack of cation exchange capacity and it has a hydrophobic character after activation.

Table 2.4. Trends in the properties of zeolites as a function of the Si/Al ratio (Van Der Waal and Bekkum , 1998)

Zeolite type	A	X	Y	MOR	MFI	Silicalite-1
Si/Al (minimum)	1	1	2.5	5	10	∞
	←		Number of cations			
			Stability vs. acidic solutions		→	
			Acid strength zeolite proton		→	
			Thermal stability			→
	←		Hydrophilic character			
			Hydrophobic character			→
	←		Affinity for polar molecules			
			Affinity for apolar molecules			→

2.4 Natural Occurrence of Zeolite

Zeolite minerals are known to be distributed rather unevenly in Nature. According to Clifton (1987), zeolite formed in various condition and geological system. This is also supported by Iijima (1980) which reported that zeolites formed in various sediment or rock under varying physical and chemical environment. Genetic classification of occurrence has been attempted by some workers such as by Hay (1978), Iijima (1978), Iijima and Utada (1966), Gottardi and Obradovic (1978) and Mumpton (1973). Much work in the field or in the laboratory has been proved in several studies about the importance of temperature towards zeolite formation. In addition to that, it is also proved by Hay (1978), Surdam and Sheppard (1978) and Kastner and Stonecipher (1978) the significant role of pore water chemistry which helps zeolite to precipitate. As a result of the geothermal or chemical gradient, zeolites commonly occur in a vertically or laterally zonal arrangement which also known as zeolite zones. Therefore, according to Iijima (1980), temperature and nature of pore water should be emphasized as the criteria to classify the genetic occurrence of zeolite.

This classification is shown in Table 2.5. Meanwhile, Figure 2.6 and figure 2.7 shows the schematic representation of spatial zoning for zeolitizing system of the genetic kind (Hay, 1978 and Barrer, 1982).

Table 2.5. Genetic types of occurrence of zeolite (Iijima, 1980)

A	***Zeolites form at the elevated temperature, the zones being primarily caused by geothermal gradient***
	1. Magmatic primary zeolite
	2. Contact metamorphism
	3. Hydrothermal
	4. Burial diagenesis (or metamorphism)
B	***Zeolites form at or near the surface condition, the zones being principally caused by chemical gradient.***
	5. Percolating groundwater
	6. Weathering
	7. Alkaline, saline lake deposits
C	***Zeolites form at low temperature, any zones being not recognized***.
	8. Marine environment
D	***Zeolites form in impact craters***.
	9. Impact crater

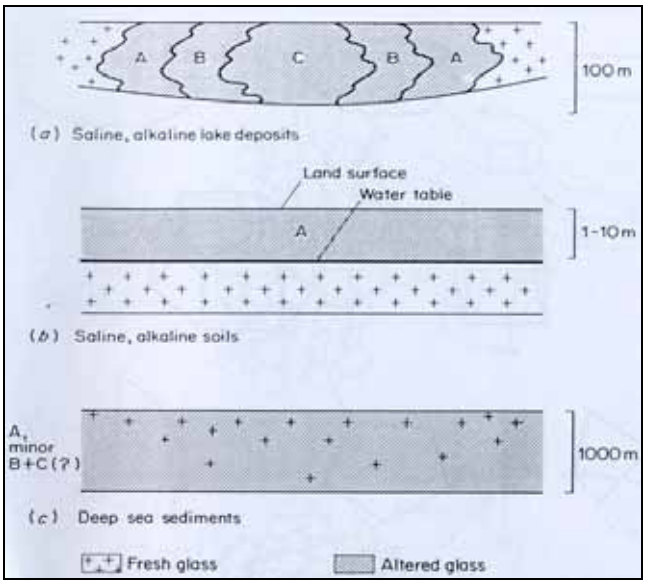


Figure 2.6. Zoning patterns of zeolites and feldspars in tuffs of saline, alkaline lakes; and deep sediments. Zone A contain alkali-rich zeolites excluding analcime; zone B contains analcime; and zone C contains feldspars (Barrer, 1982)

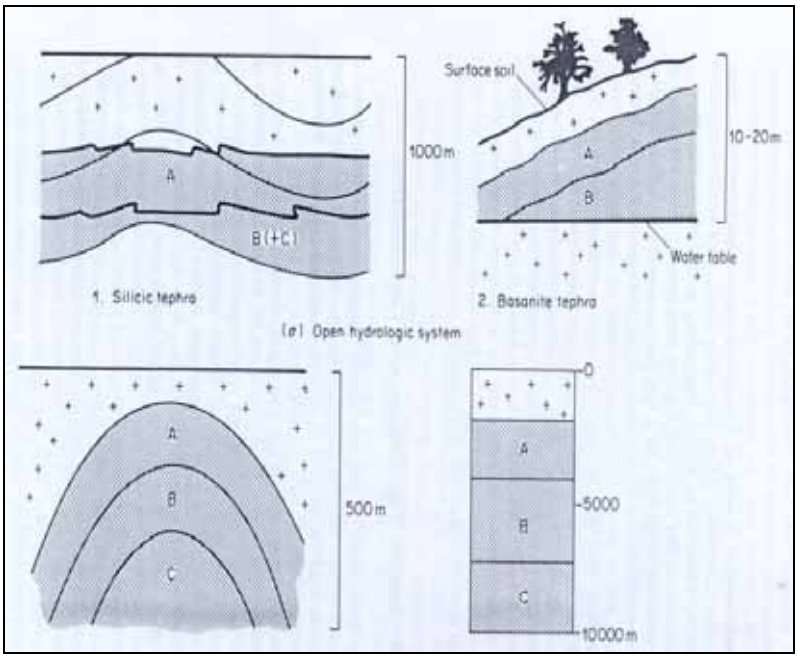


Figure 2.7. Zoning patterns of zeolites and feldspars in tuffs where zonation is (a) of open system type; (b) hydrothermal; and (c) a result of the burial diagenesis. Zone A is characterized by non-analcime alkali-rich zeolite; zone B by analcime or heulandite; and zone C by K-feldspar in (a) and albite with or without laumontite in (b) and (c).The symbols are the same as in Figure 2.6 (Barrer, 1982)

2.5 Synthesis of zeolite

The efforts to synthesize zeolite can be traced back as early as in year 1848 when Wöhler first recrystallized apphophylite which was carried out by heating it in water solutions at 180-190°C under 10-12 atm. Followed by this, several attempts were made during the 1860s and Claireveille becomes the first man to synthesis levynite via hydrothermal method in the laboratory. Unfortunately, it was pointed out by Barrer (1983) that the data for the synthesis is not in details. It was only during 1940s that zeolite syntheses get great attention, thanks to Barrer, Milton and co-workers for their pioneering work. Even now, the area of zeolite synthesis is still expanding, and as a result, synthetic zeolites with new topologies and new catalytic sorption and

separation properties are discovered. Byrappa and Yoshimura (2001) reported that there are three general processes used to produce zeolite. There are as below:

1. Preparation of molecular sieve zeolites as high purity crystalline powders.
2. The conversion of clay minerals into zeolites.
3. Processes based on the use of other naturally occurring raw materials.

Due to the industrial important of this mineral, much effort is made to unravel the mechanism responsible for its formation from its precursors. The art of creating zeolite synthesis has become a scientific interest because this concept may be derived for tailor-made zeolite synthesis. As we know, aluminosilicates zeolites synthesis involves mixing together Si and Al species, metals cations, organics molecules and water, which are then treated hydrothermally and the mixture then is then converted into a microporous crystalline aluminosilicate. This process also can be denoted as zeolitization.

Since the 1940's, systematic studies on zeolite synthesis have been disclosed. It was reported (Barrer, 1982) that the first zeolite which did not have a natural counterpart has been synthesized. Then, during the late 1940's, a group of Barrer and Milton has initiated zeolite technology on a large scale. They have synthesized zeolite via hydrothermal synthesis using reactive alkali-metal aluminosilicate gel at low temperature (~100°C) and pressure (autogenous). This is illustrated schematically in Figure 2.8 where the starting materials (Si-O and Al-O bonds) are converted by an aqueous mineralising medium (OH- and/or F-) into the crystalline product (Si-O-Al bonds) whose microsporosity is defined by the crystal structure (Cundy and Cox, 2005).

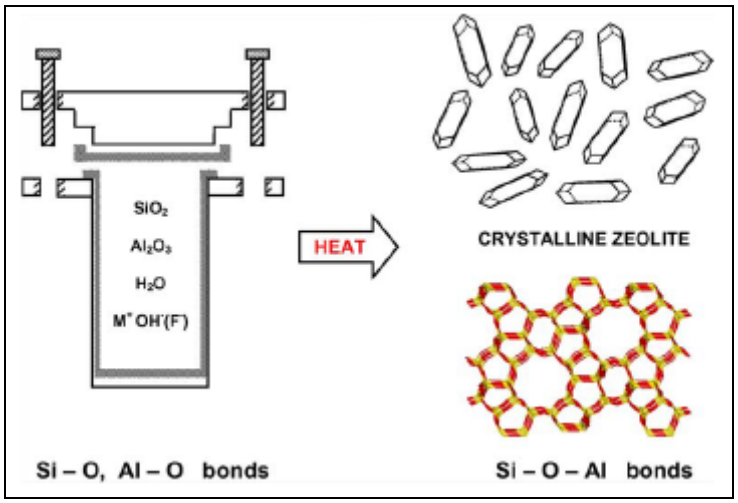
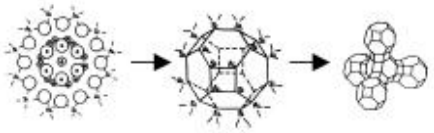
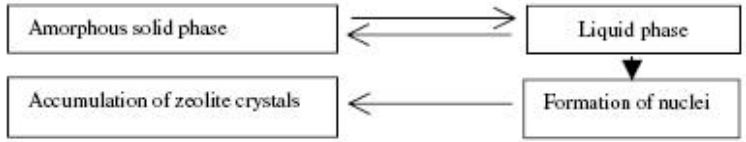
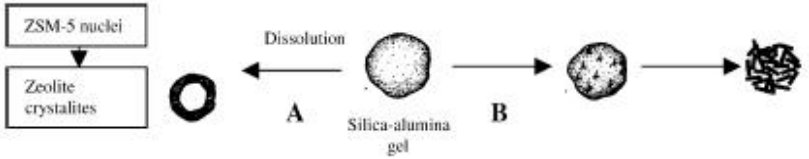


Figure 2.8. Hydrothermal zeolite synthesis (Cundy and Cox, 2005)

Several literatures reported that by 1958, under Milton's leadership, the Linde Division of Union Carbide has successfully synthesized nearly all the important commercial zeolite (Milton,1989; Rabo and Schoonover, 2001; Cundy et al., 2003). From Cundy and Cox (2005), a summary of principal proposal for zeolite synthesis mechanism since 1959 to 2004 is listed in Table 2.6.

Table 2.6. Summary of principal proposals for zeolite synthesis mechanism, 1959-2004 (Cundy and Cox, 2005)

Author(s)	Principal system studied	Main features of mechanism	Schematic summary
Barrer	Various low-silica phases	Condensation polymerisation of polygonal and polyhedral anions	
Flanigen and Breck	Na-A, Na-X	Linkage of polyhedra (formed by M^+-assisted arrangement of anions): crystal growth mainly in the solid phase	
Kerr	Na-A	Crystal growth from solution species	Amorphous solid $\xrightarrow{\text{fast}}$ soluble species(S) (S) + nuclei(or zeolite crystals) $\xrightarrow{\text{slow}}$ zeolite A
Zhdanov	Na-A, Na-X	Solid ↔ liquid solubility equilibrium, nuclei from condensation reactions, crystal growth from solution	
Derouane, Detremmerie, Gabelica and Blom	Na,TPA-ZSM-5	Synthesis "A": liquid phase ion transportation. Synthesis "B": solid hydrogel phase transformation	
Chang and Bell	Na,TPA-Si-ZSM-5	Embryonic clathrate TPA-silicate units, ordered into nuclei through OH^--mediated Si—O—Si cleavage/recombination	
Burkett and Davis	TPA-Si-ZSM-5	Pre-organised inorganic–organic composites, nucleation through aggregation, crystal growth layer-by-layer	
Leuven Group	TPA-Si-ZSM-5	Oligomers → precursor "trimer" (33 Si) → ×12 → "nanoslabs", growth by aggregation	

2.6 Application

Zeolites have basically found a wide array of applications due to their applicability in almost all fields of human life where chemical; biochemical and physicochemical processes are taking place. They can be used for purification of gaseous as well as liquid mixtures and solutions by sorption, for storing of molecules, for sieving and filtering, for ion exchange purposes and also for catalysis under non-oxidizing and oxidizing environment. The uses for zeolites are generally categorized into three functional classifications, and within each function exists a broad range of applications as below.

2.6.1 Zeolite in adsorption and separation

The basis for the usage of zeolite in gas adsorption is due to the shape-selectivity properties. The ability to preferentially adsorb certain molecules while excluding others has opened up a wide range of molecular sieving applications. Sometimes, it is simply matter of the size and shape of pores controlling access into the zeolite. In other cases, different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by silicalite.

Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also to find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with metal ions. Conversely, hydrophobic silica zeolites preferentially adsorb organic solvents. Thus, zeolites can be used to separate molecules based on the differences of size, shape and polarity. The use of zeolite in some application of adsorption and separation is stated as follows:

(a) Odour control

Zeolites are used in a wide range of consumer products to remove both moistures and odours. They have a large capacity for moisture absorption and can be re-used many times by simply heating to remove absorbed moisture. They also absorb undesirable odours and have many useful applications in the home. Some of the examples of zeolites usage in this case include fridge deodorizers, shoe cupboards, wardrobes, car and boat deodorizers, elimination of pet odours. In fact, zeolites can be used in almost any situation and problem where moisture and/or odours are involved. They are totally harmless to humans and animals, and can be re-used over and over again.

(b) Industrial gas separation and purification

Synthetic zeolites have been used for many years in the petroleum industry, but natural zeolites are being increasingly used as a cost effective alternative in certain applications where there is no performance disadvantage. Natural zeolites are particularly effective in the following applications: Removal of water and carbon dioxide from gaseous hydrocarbons, removal of hydrochloric acid from gas streams, removal of hydrogen sulphide from gas streams and catalysis and natural gas separation.

(c) Water adsorption/desorption

Zeolite is a mineral which has a high affinity for water and has the capability of adsorbing and desorbing it without damage to the crystal structure. This property makes them useful in desiccation as well as other unique commercial application